A Method for Improving Nucleation of Thick YBCO Films in the *Ex-Situ* Process

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Abstract—Some coated conductor applications require a YBCO layer at least 5 μm thick with high J_c. The growth of thick c-axis oriented epitaxial layers using the barium fluoride *ex-situ* technology is not always possible. Films over 3 μm thick have more undesirable a-oriented and random grains than thinner ones. We present an analysis of thick film nucleation and conclude that thick precursor layers impede out-diffusion of the *ex-situ* reaction product, HF. High impedance for HF diffusion results in large variations of the chemical potential of the growth reaction and disruption of the nucleation process. We conclude that a solution for c-axis growth is control of the precursor permeability. A method is described for controlling the permeability of precursor layers. Using this technique we were able to grow c-axis oriented 5-μm thick films on oxide-buffered Ni tape with $J_c(0 \text{ T}) = 4 \times 10^5 \text{ A/cm}^2$ and $J_c(1 \text{ T}) = 8 \times 10^4 \text{ A/cm}^2$.

Index Terms—Barium fluoride process, coated conductors, YBCO.

I. INTRODUCTION

YBa$_2$Cu$_3$O$_7$ (YBCO) has long been considered a promising candidate for second generation coated HTSC conductors. However, for some applications, the YBCO conductors should possess high engineering current $J_e = 10^4$ A/cm^2. Taking into account the thickness of the metallic substrate (50 –100 μm), thickness of the insulation and conductive overcoat needed for conductor stability, this requirement translates into a critical current density, J_c, of about 1 MA/cm^2 for an YBCO layer with a thickness of 5 –10 μm. While critical currents well over 1 MA/cm^2 were demonstrated for YBCO layers up to 1 μm thick, prepared by both *in-situ* [1] and *ex-situ* techniques [2], growing several micron thick layers with high J_cs has turned out to be a challenge. For instance, the critical current of YBCO layers deposited by pulsed laser ablation (PLD) dramatically decreases with the layer thickness. It was found that YBCO material deposited over a critical thickness of about 1.5 μm has negligible contribution to the overall critical current of the conductor [3]. The *ex-situ* process has a similar limitation, that is, films thicker than 1 micron tend to have a large amount of a-oriented (a-axis perpendicular to the substrate face) and random grains. These grains are the source of high angle boundaries that lower the critical current. However, unlike PLD films, thick *ex-situ* processed films have a high content of a-axis and random

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grains starting from the substrate interface. Therefore the precursor thickness negatively influences the nucleation process. Understanding this effect is important for many applications of the *ex-situ* process. In this paper we will address this problem.

II. EXPERIMENT

Precursor films of the approximate stoichiometric cation composition Y : Ba : Cu = 1 : 2 : 3 were deposited onto oxide buffered RABITS tapes, which had the structure Ni-CeO$_2$-ZrO$_2$-CeO$_2$. The Y and Cu were deposited using Temescal 14 kW electron beam guns and a custom 300 W thermal evaporation source was used to deposit the BaF$_2$. The deposition rate was 14 nm/s as calculated for the thickness of annealed YBCO films. The background pressure in the chamber was 1 –2×10^{-6} Torr during deposition and the deposition rates of the individual sources were controlled by Inficon quartz crystal rate monitors.

Post deposition annealing was performed in a quartz tube. The annealing atmosphere was synthesized by mixing certified gases using electronic mass flow controllers. The total gas flow was fixed at 100 sccm and was humidified by bubbling through a heated water bath. The humidity was measured with a capacitive sensor and active feedback was used to stabilize the water vapor partial pressure by varying the water bath temperature.

The oxygen partial pressure was preset at 100 mTorr and the processing temperature was 735°C. The growth rate was determined from the *in-situ* conductivity of the film sample as described in [4].

III. THERMODYNAMICS OF EPITAXIAL NUCLEATION

First we briefly discuss some aspects of YBCO *ex-situ* nucleation, concentrating primarily on how the precursor thickness can influence nucleation. Classical models of solid phase epitaxial nucleation describe the process as formation of critical nuclei from a supercooled parent phase, which can be vapor, liquid or another solid. The energy of the nuclei, E_n, is

$$E_n = E_s + E_v \tag{1}$$

where E_v is the volume energy and $E_v \sim \sigma r^3$, where r the nuclei radius and σ the supersaturation. We use the following definition of supersaturation: $\sigma = \Delta\mu/k_B T$, where $\Delta\mu$ is the change of the chemical potential per unit cell as a result of crystalline phase formation (YBCO) from the parent phase (fluorinated precursor), k_B is the Boltzmann constant and T the growth temperature. The surface energy, E_s, is proportional to the area of the nuclei, that is $E_s \sim r^2$.

Nucleation requires a critical nucleus big enough to be thermodynamically stable. The bigger the required nuclei are, the lower the nucleation probability and the nucleation step requires

more time. However, once such a nucleus is formed, it can grow quite rapidly since crystallization kinetics or supply/removal of the reaction components/products limits its growth. The critical nuclei grow and merge into a bulk crystalline phase. The size of the critical nucleus, r^*, and energy required to create it, E_n^*, are determined by maximization of $E_n(r)$ in (1). At low σ values the surface dominates over the volume and the critical nucleus is large and epitaxial. As σ increases, the volume term becomes more important and the critical nucleus gets smaller. When the size of the nucleus becomes smaller that the unit cell, epitaxial growth is not possible and the material crystallizes as randomly oriented grains i.e., polycrystalline

Therefore, as a general rule, growth of high quality epitaxial layers requires large critical nuclei, which implies low supersaturation. Due to the large size of the nuclei, growth at low supersaturation is more predicable since it is less sensitive to substrate imperfections and local composition variations. Applying this rule to YBCO processing, it may be concluded that growth of c-axis oriented YBCO requires a low growth rate and low oxygen partial pressure. This rule is found to be true for many *ex-situ* and *in-situ* deposition techniques.

IV. COMPETITION OF EPITAXIAL MODES DURING *EX-SITU* NUCLEATION

In the *ex-situ* process supersaturation depends upon the partial pressure of HF, $P(HF)$, at the growth front,

$$\sigma = \ln\left(\frac{P(HF)}{P(HF)_e}\right) \qquad (2)$$

where $P(HF)_e$ is the equilibrium HF partial pressure related to the water vapor partial pressure [4]. It was shown previously [4] that under typical growth conditions $P(HF) \approx P(HF)_e$ and σ therefore is comparatively low. It is surprising that at growth rates of 0.1–0.2 nm/s, which is much lower than for an *in-situ* process (e.g., typical growth rates for laser deposition, 1–10 nm/s), a-axis and random nucleation are often encountered in *ex-situ* processed films. Another paradox is influence of precursor film thickness on film nucleation. It would appear that a thicker film would impede HF out-diffusion, making growth even slower, which is beneficial for c-axis, oriented YBCO. This is opposite to the experimental observation that it is very difficult to grow c-axis oriented YBCO films thicker than 5 microns.

We believe that the gradient of the supersaturation is a factor, which should be also taken into account to explain the effect of thickness. To introduce the gradient term we replace σ with $\sigma + L\partial\sigma/\partial n$, where $\partial\sigma/\partial n$ is the gradient of σ normal to the face of the film and L is the size of the nuclei in this direction. According to (2) the supersaturation gradient is determined by the HF diffusion profile in the precursor solid and the processing atmosphere. The thicker the film is, the larger the gradient due to increased impedance to HF out-diffusion. Therefore a-grains, which can grow rapidly in the direction normal to the film surface, can take advantage of the $\partial\sigma/\partial n$ term. In sufficiently thick films $\partial\sigma/\partial n$ can become large enough to make a-axis and even random nucleation thermodynamically possible. Generally, the transition from c to a growth can be described as a topological change of the growth front from smooth boundary (c-growth) to a serrated one (a-growth). Such transitions are well known for zone-melting processes, where high $\partial\sigma/\partial n$ values occur due to high temperature and concentration gradients in the melt zone [5].
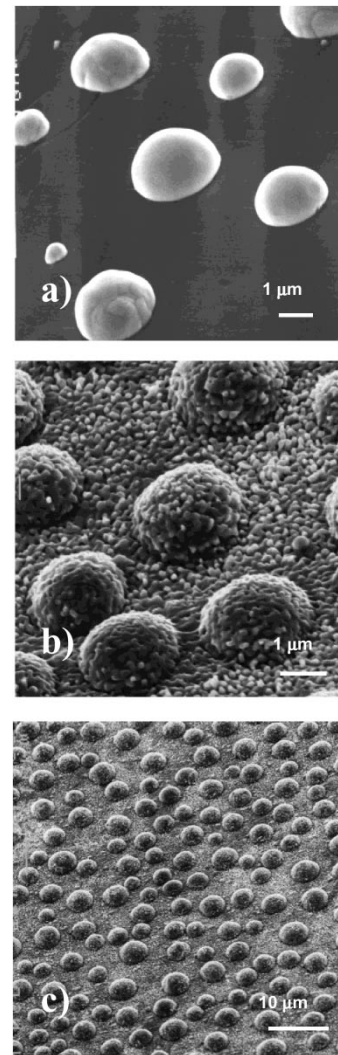

Fig. 1. SEM micrographs: (a) RABITS substrate with Ag microspheres. (b) and (c) 3 μm YBCO deposited on substrate shown in (a).

This phenomenon seems to be intrinsic to the *ex-situ* process, where spatial variations of σ are determined by HF removal by (slow) solid-state diffusion through the precursor. In comparison, during *in-situ* growth, the film surface is in contact with a gaseous atmosphere, where rapid gas-phase diffusion makes such gradients negligible.

Differentiating (2) we find that $\partial\sigma/\partial n = 1/l$, where l is the distance over which a substantial HF pressure drop occurs. Assume, for example, the impedance for HF out-diffusion through the solid precursor film is I_s, and the impedance of the processing atmosphere is I_a. In the limiting case of a highly permeable precursor film where $I_s \ll I_a$, l is equal to the film width, which is about 0.1–1.0 cm. In the other limit where the precursor is less permeable than the processing atmosphere and $I_s \gg I_a$, l is equal to the sample thickness, $\approx 10^{-4}$ cm. We speculate that the second limiting case corresponds to a-axis and random nucleation in thick films.

An obvious solution would be to increase I_a, decreasing the growth rate, to match the larger I_s value. Unfortunately, for reasons yet unknown, the film quality degrades at very low growth rates.
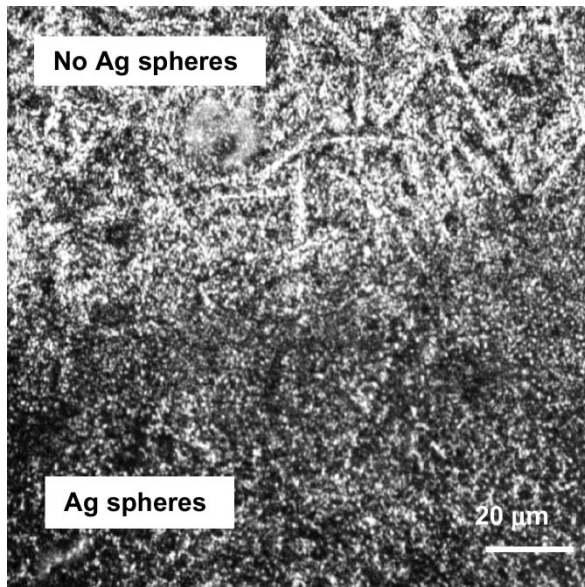
Fig. 2. Optical micrograph of 5 μm thick film on RABITS tape. Upper part has no silver microspheres deposited on the substrate.

V. APPLICATION OF SILVER MICROSPHERES FOR MODIFICATION OF THE FILM PERMEABILITY

It follows from our analysis that the growth of thick films requires control over the film permeability. That is, the permeability should be decreased in thick films to compensate for the thicker precursor layers. Vacuum-deposited films appear quite dense and the "natural" porosity of such samples is quite low. We proposed and realized a solution to the problem using arrays of silver microspheres or dots. As the first step a layer of silver, up to 1 micron thick, is deposited on the substrate. The substrate is very briefly heated in an atmosphere of forming gas (4% H_2–96% N_2) up to the melting temperature of silver, 960°C. This causes the silver layer to melt and coagulate into an array of microspheres. The density and size of the microspheres is roughly proportional to the silver layer thickness. YBCO precursor is next deposited on the microsphere coated substrate by vacuum evaporation. Fig. 1 is a SEM micrograph featuring the steps of the process. Fig. 1(a) shows a RABITS substrate after deposition of silver dots. Fig. 1(b) and (c) show the same substrate after 3 μm thick YBCO had been deposited by vacuum evaporation. During the evaporation the silver dots act as shadows for the on-coming vapor and create an ordered network of vertical channels. These channels work as vents, facilitating out-diffusion of HF and significantly improving the nucleation. Fig. 2 is an optical micrograph, which illustrates the influence of the silver dots on the surface morphology of a 5 micron thick film deposited on a buffered RABITS substrate. The substrate has been masked during deposition of the silver film layer so that a part of the film did not have the silver dot array on the surface. As can be noticed from the figure, the part of the tape not covered with silver has large amounts of random grains that are absent in the part of tape covered with silver. The presence of the silver dots suppresses random nucleation. X-ray diffraction confirms this observation. Using this technique we were able to grow completely c-axis oriented 5 micron thick films on a buffered RABITS substrate. The film
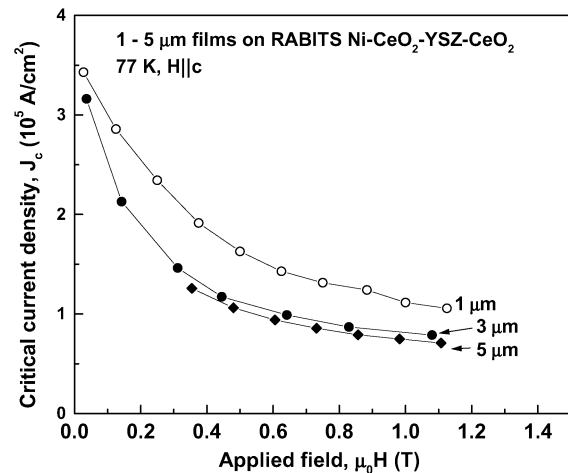

Fig. 3. Critical currents of 1, 3, and 5 μm thick YBCO films on RABITS buffered tape. Films of 3 and 5 μm thick were prepared using the silver dot technique.

had $T_c = 91$ K. We typically obtained $J_c(0\,\text{T}) = 0.4\,\text{MA/cm}^2$ and $J_c(1\,\text{T}) = 0.8 \times 10^5\,\text{A/cm}^2$ for a 3–5 μm thick films on RABITS substrates. The critical current field dependence ($H\|c$) of 5 and 3 micron thick films prepared using the silver dot technique are presented in Fig. 3. In the same figure the critical currents of these films are compared with the J_c of a 1 micron thick film without silver microdots. The figure illustrates a downside to the technique. The silver dots reduce the effective cross-section of the superconductor by approximately a factor of 2. We believe this is the reason why the critical current densities of the 3 and 5 μm thick films in Fig. 3 are roughly two times lower than the J_c of the 1 μm thick sample.

VI. CONCLUSION

In conclusion, we believe the high impedance to HF out-diffusion through the precursor layer is the primary reason for the poor c-axis nucleation of *ex-situ* processed YBCO thick films. We have demonstrated a concept employing vertical diffusion channels created using an array of silver microdots. The diffusion channels lower the impedance to HF out-diffusion resulting in almost complete c-axis growth of 5 micron thick YBCO films.

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